## REMARKS/ARGUMENTS

### Restrictions

The Examiner has raised a restriction requirement. Please note that claims 1 to 20 were subject to an International Search Report (claims 16 to 19 of the application as filed are the same as the claims 17 to 20).

The US as a Contracting State of the PCT has agreed pursuant to the Report of the PCT Assembly 18th Session

"that designated Offices should not raise an objection to lack of unity if no

such opinion is expressed in the International Search Report".

We enclose a copy of the relevant page from the PCT handbook from which the above passage is quoted.

Accordingly the restriction requirement for claims 17 to 20 (corresponding to 16 to 19) subject to the ISR is an objection to lack of unity, and should be withdrawn.

Further the formation of the product in aqueous solution is relevant to the nature and properties of the product. This is apparent from the contrast between the prior art and the invention discussed later in this response. We also consider that the restriction requirement is rendered moot by the proposed claim amendments.

As affirmation of an election is required we hereby confirm the provisional election of Group I claims made in the telephone conference with Mr Peter Cronk on 14 October 2003. Claims 1-16 and 21-23 are readable on Group I.

## WO 97/14750

As acknowledged by the Office Action, this document does not relate to radiation curable resin compositions and does not disclose or suggest curing of the resins by UV or electron beam radiation.

The problem addressed by WO 97/14750 is described in the paragraph bridging pages 1 and 2. The conventional epoxy resin compositions for coating metals contain curing agents and are poorly stable, require high temperature, long reaction steps and are difficult to control. The citation specifically addresses problems of <u>thermal</u> curing.

The resin system disclosed in the citation is a thermally polymerised resin. This is clear not only from the introduction but is explicitly stated on page 16 lines 2 to 21:

"Next, a radical polymerisation initiator is added to the thus-obtained dispersion...........and then heated, whereby the unsaturated compound in the aqueous dispersion is polymerised.

The polymerisation is effected generally at a temperature falling between $50^{\circ}C$ and $100^{\circ}C$ for from 15 minutes to 3 hours......."

This document then refers to the strong preference for using an inert gas in order to efficiently promote the reaction and lists a range of <u>thermal</u> polymerisation initiators.

The use of amine adducts in a UV polymerisable composition is contrary to the plain teaching of the '750 application which addresses thermally polymerisable coatings and explicitly recites the conditions and components to be used which provide thermal polymerisation.

As explained in the Polymer Update paper (cited under 35 USC 103 and discussed below) photopolymerisation and thermal polymerisation are not merely interchangeable techniques.

The rejections under 35 USC §102 and §103 should be withdrawn for reasons as illustrated by the comparative examples of the citations. The comparative examples show that unless the specific reaction sequence described in the claims was followed the compositions containing thermal polymerisation initiator gelled and would not be suitable as a water soluble resin composition. Comparative Examples 2 and 3 show the critical importance of the addition of ammonia or other neutralising agent to the composition after initial reaction in the presence of the thermal polymerisation initiator.

The whole teaching of the document is clearly specific to thermally cured systems. In contrast the present inventors have found that a radiation curable composition having a prepolymer formed between an unsaturated carboxylic acid and specific amine oligomer enable UV curing to occur without the need to use photoinitiators in many instances.

Further in striking contrast to the teaching in the citation to use inert gas to obtain efficient reaction, the present inventors have found that their UV polymerisable resin can be radiation polymerised in air.

## US 4253918 – (Traenckner)

Traenkner unlike the present invention is not concerned with amine salt prepolymers. This is clear from Traenckner because Traenckner uses organic solvents as the reaction and not water as required by amended claim 1. Indeed Traenckner teaches a process in which an amine is reacted with a portion of the epoxy groups and then an ester product is formed by reaction of an unsaturated acid with the remaining epoxy groups.

Thus, in column 4 line 19 to 24 Traenckner teaches reacting from 0.01 to 0.05 (preferably 0.05 to 0.3) NH equivalents (see line 19) of ammonia or amines per epoxy equivalent in an <u>inert solvent</u> (see line 28).

The remaining epoxy group of the amine reaction product are reacted with acrylic and/or methacrylic acid. Thus in lines 48 to 53 Traenckner teaches:

"Reaction of the polyepoxides with the nitrogen compounds if followed by reaction of the resulting products with acrylic and/or methacrylic acid. 0.5 to 0.99 carboxyl equivalents and preferably 0.7 to 0.95 carboxyl equivalents of (meth)acrylic acid are used to one epoxide equivalent.".

The fact that Traenckner is forming an ester rather than salt is made manifest by Traenckner's reference to use known methods referred to in US 3301743 and US 2824853.

Each of these patents, copies of which are enclosed, condense an acid with an epoxide to form an ester i.e.
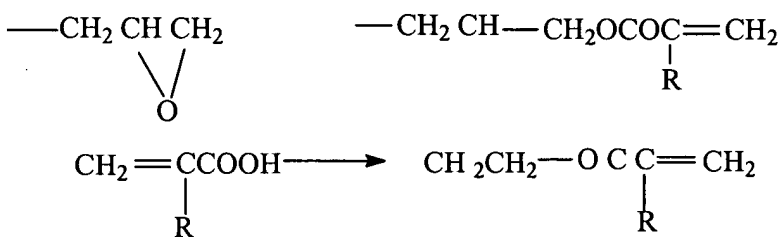


In contrast, the present invention requires reaction of an amine salt prepolymer with an unsaturated acid in water. Water in this context is the antithesis of inert solvent required by Traenckner because, as one skilled in the art can appreciate, water reacts rapidly with epoxy groups.

In the present invention the unsaturated acid is therefore left to form a salt with the

$$CH_2\ CH\ CH\ \overset{\displaystyle H}{N}\ R^1\ R^2$$
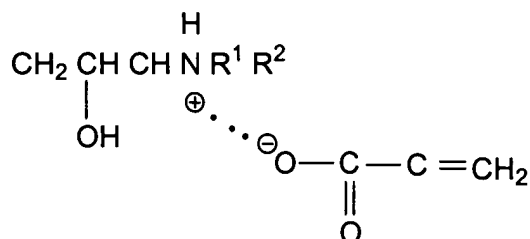
condensed amine.

In order to examine the product of Traenckner the present inventors repeated Example 2 of Traenckner. Example 2 was chosen as the representative example because it uses the secondary amine diethanolamine of the same general type as may be used in the present invention. When the procedure of Example 2 was repeated the resulting polymer product was found to be completely water insoluble but soluble in monomers and organic solvents as reported by Traenckner.

## Polymer Update: Science and Engineering

The generation of free radicals by UV radiation of monomers is limited to specific groups of monomers and it would not suggest to one of ordinary skill in the art that, because free radicals can be generated from a wide range of monomers, it would be obvious to use any and all specific monomers in a UV curable system. Indeed, as explained in the introduction to the present invention, the resin systems used in industry are limited almost exclusively to certain types.

The attached extract from the authoritative book "Chemistry and Technology of UV and EB Formulations for Coatings, Inks and Paints", explains some of the difficulties faced in formulating UV curable compositions for use in industry. On page 9 the book explains the technical limitations in obtaining useful industrial radiation curing. In particular in the

portion of this page which has been highlighted, the text explains that although unsaturated oligomers and monomers in UV curable systems are capable of absorbing UV radiation, the rate at which they do so and the rate of any subsequent polymerisation for film formation are "so slow as to make this process uneconomic and technically unacceptable". The book authority therefore concludes that it is necessary to add photo-initiators or photo-sensitisers in order to obtain a useful rate of polymerisation.

This is also explained on page 1 of the present application which identifies the classes of photo-initiators which are generally required to achieve effective polymerisation.

In contrast to the accepted practices in the art of using significant concentrations of photo-initiator, the present inventors found that when certain select types of resin compositions are used, the resin composition is surprisingly sensitive to UV radiation. Indeed as explained in the present application, in many cases the use of a photo-initiator can be dispensed with altogether. The photo-initiators used in the prior art compositions are generally relatively expensive when compared with the other components of UV polymerisable compositions. The finding that specific groups of resins, which are quite different to those conventional used, allow the use of initiators to be significantly reduced and even dispensed with therefore has enormous industrial significance.

Another problem of conventional systems which is identified in the attached paper is the quenching of the radical reactions by oxygen. The finding of the present inventors that the compositions of the invention cure well in air without this significant inhibition by oxygen is also of significant industrial importance.

In summary, the reliance by the rejection on this document to suggest that it would be obvious to cure monomers by UV radiation is based on oversimplification of factual evidence in the prior art. It ignores the fact that resin systems must be specifically designed to cure efficiency by an initiation process.

Further as explained in the above discussion of ('750) that citation specifically addresses thermally cured resins. Neither a UV initiator nor the use of UV light is suggested by '750 and this would be contrary to the teaching of '750 which requires a thermal initiator and thermal curing.

From the foregoing amendment and Remarks supporting patentability, allowance is respectfully requested.

Respectfully submitted,

Dated: _1·22·04_

Gerald K. Kita
Registration No. 24,125
Attorney For Applicant

DUANE MORRIS LLP
One Liberty Place
Philadelphia, PA 19103-7396
(215) 979-1863 (Telephone)
(215) 979-1020 (Fax)

Attachments:  Copy of page from PCT handbook;
Copy of US 2,824,851 and US 3,301,743;
Copy of paper.

PCT Contracting States in an international application. Nevertheless, there may be occasions when it would be wise to include individual groups of claims drafted in accordance with the practice before one or more of the designated PCT Contracting States or the designated Offices, such as the U.S. patent office and the EPO, so long as all the claims are consecutively numbered as a single series. Such an occasion could arise for designated PCT Contracting States where the so-called provisional protection arising on publication is important to the applicant. Such provisional protection is discussed at paragraph 14.4. An occasion to include, on filing an international application, claims drafted in accordance with national practice could also arise if the risk of adding new matter when presenting such claims later is to be avoided. Accordingly, during international preliminary examination under Chapter II PCT, the examiner should not adopt an overly academic or rigid approach to the presence of a number of claims which are differently worded but apparently of similar effect (PCT Preliminary Examination Guidelines, paragraph III–3.2 (Appendix V of this Handbook, Section 5)). In any event, different claims, including different sets of claims, can be filed at the various designated Offices on entry into the national phase (see para. 33.19).

## 23.9    Unity of invention

The conditions for unity of invention under the Patent Cooperation Treaty are set out in Rule 13 PCT. According to the *Report of the PCT Assembly, 18th Session* (1991), item 24 (WIPO Document PCT/A/XVIII/9), the content of the version of Rule 13.2 and 13.3 PCT in force up to June 30, 1992 continues to apply and has been incorporated into the PCT Administrative Instructions, Section 206 and Annex B, Part I (Appendix III of this Handbook). Consequently, previous decisions by International Searching Authorities, finding unity of invention to be present, remain relevant. For example, there is no lack of unity in the case of an international application containing a claim directed to a process and a claim directed to an apparatus specifically designed for carrying out that process, even when the apparatus can be used for carrying out another process. Two inventions, to involve the same inventive concept, must have a common concept which is both novel and inventive. Unity of invention can be considered *a posteriori* as well as *a priori*. That is to say, the International Searching Authority can consider whether there is unity of invention in the light of prior art already found. If, in the light of the prior art there is no common inventive concept in the matter claimed, there can be a lack of unity. For an elaboration of this subject, see PCT Search Guidelines, Chapter VII and PCT Preliminary Examination Guidelines, section III–7 (Appendix V of this Handbook, Sections 4 and 5).

According to the *Report of the PCT Assembly, 18th Session* (1991), item 25 (WIPO Document PCT/A/XVIII/9), the PCT Contracting States have agreed that the Patent Cooperation Treaty provisions as to unity of invention would continue to apply in the national phase. This means that designated Offices should not raise an objection to lack of unity if no such opinion is expressed in the international search report. Conversely, such objection may be raised by

# CHEMISTRY & TECHNOLOGY
## OF
## UV & EB FORMULATIONS
## FOR
## COATINGS, INKS & PAINTS

VOLUME II

PREPOLYMERS & REACTIVE DILUENTS
FOR UV & EB CURABLE FORMULATIONS

by

N S Allan, M S Johnson, P K T Oldring, S Salim

with contributions by
R Holman, C Lowe, G G Skelhorne.

Chief Editor
P K T Oldring

# VOLUME II

# OLIGOMER & REACTIVE DILUENTS

## FOR

# UV & EB CURABLE FORMULATIONS

## CONTENTS

## The Chief Editor

Peter Oldring gained a BA in Chemistry in 1969 from York University, England.

He was, in 1973, awarded a PhD by the University of Manchester, Institute of Science and Technology.

Peter has worked, as a Senior, in the Technical Departments of various Companies associated with inks and paints and particularly resins.

He held a Senior Technical appointment with Cray Valley (then Cray Valley Products Ltd).

He has also been involved with Marketing, with Thomas Swan and Company Ltd.

He would like to acknowledge Mr. Thomas Swan's permission to edit and co-author this set of textbooks.

Peter is currently employed as the Technical Manager of SOAB (UK) Ltd.

Peter has co-authored and co-edited a number of successful textbooks for SITA Technology, intended for Senior Research and Development Chemists and Managers already working at the forefront of their technologies in the Resins and Surface Coatings Industries.

The books are also intended for Graduates new to the Industry and who must understand its technologies and fundamental chemical and physical backgrounds.

Peter has also co-authored technical papers and patents, particularly in the areas of UV Curing and Lamp Monitoring, in which his expertise is widely respected.

G.P. Birtles MA., MIPM..

All free radical radiation curable formulations require a proportion of materials containing some degree of carbon-carbon double bonds, usually activated towards polymerisation by a neighbouring group. The unsaturated materials used for radiation induced free radical polymerisation are mainly based on acrylate chemistry. These and other types, including the earliest styrene polyester systems, are discussed with the features and benefits of the various types in Chapters II and III. The former considers the higher viscosity prepolymers or oligomers and the latter the reactive diluents or monomers necessary to reduce the viscosity of a formulation to enable it to be applied. In most cases, the diluent monomers will also significantly affect the properties of the cured film and these effects are also discussed.

Oligomers or prepolymers are molecules which are intermediate in molecular weight between the units they are composed of and the resulting polymer. For radiation curable systems they are relatively simple and by normal resin standards are well defined molecules. The bulk of the oligomers currently used for radiation induced free radical curing are acrylates of epoxy resins or urethanes. The simplest representatives of these classes are the diacrylates of bisphenol 'A' diglycidyl ethers and the reaction products of hydroxy acrylates and diisocyanates.

Invariably the viscosities of the oligomers or prepolymers are too high for direct incorporation into a coating and it is necessary for a viscosity reducing agent to be incorporated.

It is possible to incorporate a reactive (copolymerisable) diluent or a non-reactive (inert) one. Solvents are sometimes added, but have generally evaporated by the time the coating or ink is exposed to radiation. The addition of solvent negates the advantage of a 100% solids, non-flammable (volatile monomers excepted) system and their use should be actively discouraged unless their addition is vital for the application. Failure to remove solvents before cure commences can lead to a film with a potential weakness in the position of the solvent molecules. Reactive diluents are the subject of Chapter III.

For any free radical reaction to occur, it is necessary for the radiation source to generate free radicals. It is in this respect that EB and UV systems differ most. An over simplified comparison between UV and EB curable formulations might be that an EB system is a UV system with the photoinitiating system (photoinitiator(s) and synergists) absent. Any residual photoinitiator or photoinitiator fragments can have detrimental effects upon the properties of the cured film. Stability can be poor, particularly if the films undergo outdoor exposure. Films may be discoloured, particularly if unwanted intermediates are formed. It is generally believed that the prime cause of odour and possibly taint, above that from necessary acrylate or other unsaturated components, is from the residual photoinitiators or photoinitiator fragments. Thus, an EB system could be considered to be "cleaner" than a UV one. A schematic representation of the differences is shown in Figure 1.

For a servicable film to be obtained from radiation curable materials, some degree of cure or polymerisation and possibly crosslinking must occur.

The definition of cure is a contentious issue and depends upon the individual. Many different definitions may be given, some of which will be practical whilst others will be theoretical. Cure and cure rate are discussed in detail in Volume IV.

It is a fact that full cure is not 0% residual unsaturation or reactivity, because this state can never be practically attained. For the purposes here, cure can be considered to be that state which gives a film which will fulfil the properties required from it, whether that state is measured by practical techniques like the thumb twist test, MEK rubs or sand dryness or analytical techniques like photo DSC or FTIR.

Electronically excited states of molecules are at the heart of all "photoprocesses". Although

Table III Some Applications of Radiation Cured Materials

Cork Coatings
Dental Bonding
Fibreglass Laminates
Glass Lamination
Glass Repair
Magnetic Recording Media
Medical
Metal Coatings
Moisture Vapour Barrier Coatings
Optical Fibre Coatings
Optical Recording Media
Paper Coatings
Photopolymers for Printing Plates and Photolithography
Photoresists for Printed Circuits and Microelectronics
Photoresists for Photochemical Machining ("Chemical Milling")
Plastic Coatings
Pressure Sensitive Adhesives
Printing Inks
Release Coatings for Paper and Film
Textile Coatings
Vinyl Flooring
Wood Coatings

Equipment for radiation curing is distinctly divided into that for electron beam or ultraviolet. The former generates electrons which penetrate the coating and in so doing some electrons transfer some of their energy to components of the coatings, which results in ions and free radicals being formed. Electrons are attenuated in air and only travel short distances (typically 2.5 to 5 cm) and as a consequence they need to be generated in a vacuum.

In contrast, in UV curing photons electronically excite molecules in a coating, which then generate free radicals or cations. Obviously, the energies of electron beams are far higher than those for photons in UV radiation. This can lead to the generation of 'X' rays which require electron beam generators to be shielded. Thus, equipment for EB curing is bulkier and more expensive than that for UV curing.

Most radiation curable systems are "solvent free" and as a result their viscosities tend to be significantly higher than those for solvent based alternatives. The chemistry of the preparation of UV and EB curable oligomers or prepolymers often results in higher viscosities than would have been expected from their molecular weights alone. This is probably due to their polarity and consequential hydrogen bonding.

The raw materials to be covered in this volume are restricted to those essentially involved in radiation induced free radical chemical reactions and are common to both EB and UV formulations. Pigments have been excluded, because they are covered in "Pigments for Ink Makers" by J.D. Sanders (published by SITA). Specific requirements of pigments and pigment selection for radiation curable systems are given in Volume IV. Additives including fillers, flow control agents, wetting agents, slip aids and matting agents are covered (where they are relevant) in formulation and other chapters.

otons are a convenient means of initiating photochemistry, the absorption of light is not quired to produce electronically excited states.

However, for UV curing it is necessary for photons to be absorbed to initiate one or more otochemical processes, which ultimately lead to the initiation of polymerisation and film :ination.
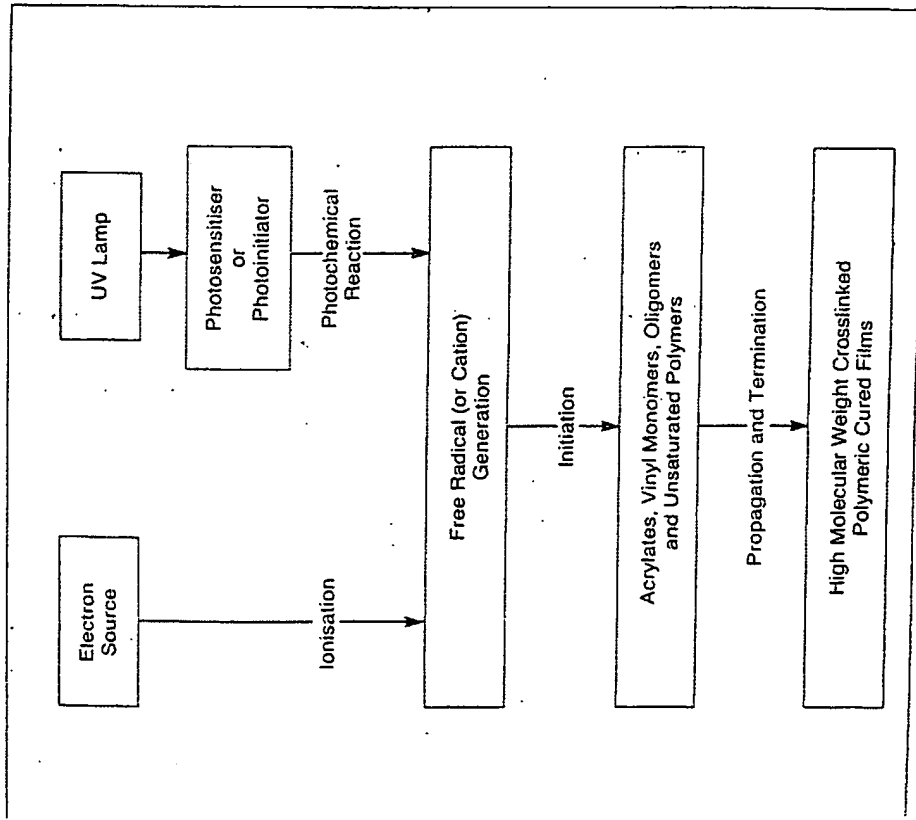
# II. ULTRAVIOLET INITIATION OF CURING

In most UV or visible light photochemical processes, energy is absorbed from a photon to form an energised or excited state. This excited state must loose its excess energy to become stable and this can be lost in one of two ways. The first involves re-radiation of energy and the second a non-radiative energy transition. In both processes excited states are inter-converted with each other or with the ground state. These processes can be called photophysical processes. As a generalisation, the net effect of light energy being absorbed is that light can be converted to light (of a different wavelength), heat or to a potentially chemically reactive moiety.

There are three basic stages in a photoreaction.

i) Absorption of a photon resulting in an electronically excited state.

ii) A primary photochemical process which may involve rearrangements in the elec-tronically excited molecules.

iii) A secondary (or 'dark') process which results from the intermediates produced from the primary photochemical process.

Whilst the unsaturated oligomer and monomer components in a UV curable system are capable of absorbing UV radiation through their ethenic unsaturation, the rate at which they do so and the rate of any subsequent photoinduced polymerisation for film formation are so slow as to make this process uneconomic and technically unacceptable. Thus, it is necessary to add one or more types of molecule which undergo photochemical reactions more readily and more efficiently than monomers or oligomers. These molecules may act alone or in combination, but the end result is photoinduced initiation of polymerisation of the oligomers and monomers. These molecules are photoinitiators. They are also sometimes called photosynergists or photosensitisers, depending upon the role they perform in photoinitiation. Any commercially viable UV process must utilise a photoinitiator system, which is usually present in the formulation at concentrations between $2-15$ wt %.

For a photoinitiator to function it must absorb electromagnetic radiation and through either an intermolecular or intramolecular interaction it must produce a reactive intermediate. In the case of a free radical polymerised system it is a free radical which is required. In the case of cationic curing it is an ion which must be generated. The reactive intermediate, which is present in relatively low concentrations compared to polymerisable material, must cause the wet film to cure. (This curing process can also occur in uncured dry films, like those used in photoresists). The reactive intermediate initiates reaction between the oligomer and monomer molecules which then continues, normally forming a crosslinked network. If the discussion is restricted to free radical induced polymerisation, then the following general approach can be used.

In the case of a UV system ultraviolet light (within the $254-400$ nm region) excites a molecule which in general terms either directly or indirectly leads to the generation of free radicals. These molecules are normally referred to as photoinitiators, even if a synergist is required to generate a free radical. The following summarises the major steps in obtaining a final UV cured coating.

Photoinitiators can absorb a photon and become excited. In so doing their electronic con-figuration is altered.



Figure 1 Comparison of EB and UV Curing

## Absorption

$$AB^\bullet + h\upsilon \longrightarrow AB^*$$

| Ground State | Photon | | Excited State |
|---|---|---|---|
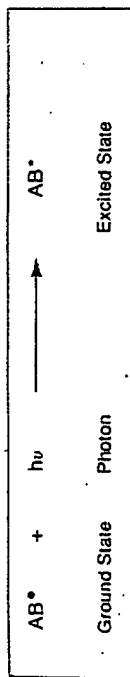
The two excited states of interest to the photochemist are Singlet and Triplet and both refer to electronic spin configuration. A configuration with no unpaired electrons is a singlet state and is typical of the ground state of most compounds. It is possible for a singlet state to exist as an excited state, because one electron can be promoted to a higher energy level orbital whilst retaining its spin. Thus, the two single electrons in different energy levels of opposite spin remain paired. In a triplet state there are two unpaired electrons of the same spin. A triplet state cannot be directly formed from a singlet ground state. The converse is also true. Photochemists use the term "spectroscopically forbidden" to refer to this situation. Although these transitions are forbidden, they can and do occur, because the singlet and triplet states are not pure states, but have a little of each other's characteristics. This is discussed in Volume 1. It is necessary for spin inversion or intersystem crossing to occur for a triplet state to be formed. The triplet state has a much longer lifetime than the corresponding singlet state. Thus, the excited triplet state is more stable than the excited singlet state and, having a longer lifetime, it is more likely to react with its surrounding molecules thereby initiating polymerisation. In essence, the triplet state produces the most useful photochemical reactions, as far as the UV coating chemists are concerned.

For most (but not all) photoinitiators used in UV radiation induced free radical curing technology, the carbonyl or activated carbonyl groups are the moieties which are involved in the primary photochemical processes.

There are a number of ways the excited state can loose its energy. Some do not lead to photoinitiation. Energy can be lost by fluorescence and phosphorescence with the excited molecule returning to its ground state.

## Fluorescence. — Light Emitted During Irradiation

$$AB^*_S - h\upsilon' \longrightarrow AB^\bullet$$

| Singlet State | | Ground State |
|---|---|---|
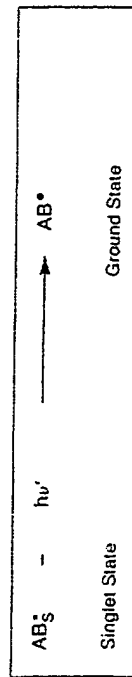
## Phosphorescence — Light Emitted After Irradiation by the Slow Decay of the Triplet State

$$AB^*_T - h\upsilon'' \longrightarrow AB^\bullet$$

| Triplet State | | Ground State |
|---|---|---|
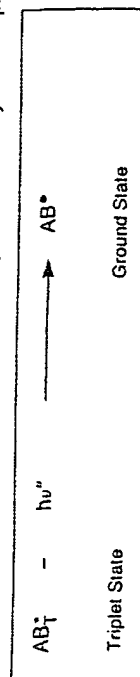
Energy can be lost or transferred to another moiety totally deactivating the excited molecule. If the moiety takes no further part in any reaction, then the moiety has quenched potential photoinitiation.

## Quenching

$$AB^*_T + Q \longrightarrow Q^\bullet + AB^\bullet$$

| Triplet State | Quenching Molecule | | | Ground State |
|---|---|---|---|---|
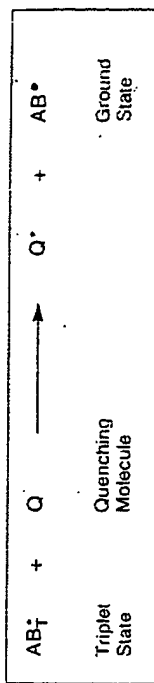
An excellent quenching molecule is oxygen, which can inhibit potential radiation induced polymerisation at all stages. At this stage, the excited molecule is deactivated by oxygen. Later in the polymerisation stage, oxygen interferes with the free radicals by trapping them and inhibiting polymerisation.

As described by Hanrahan[2] and others,[3] molecular oxygen is a di-radical with the singlet state being unstable. The triplet state is molecular oxygen's electronic ground state. The di-radical lacks the energy to initiate polymerisation and is considered stable. However, it readily reacts with existing radicals and in so doing goes from its triplet to singlet state which is unstable and readily reverts back to its di-radical state.

## Oxygen Quenching

$$AB^*_T + O_2(T) \longrightarrow O_2(S) + AB^\bullet$$

| Triplet State | Triplet | | Singlet | Ground State |
|---|---|---|---|---|

$$O_2(S) \longrightarrow O_2(T)$$

| Singlet | | Triplet |
|---|---|---|
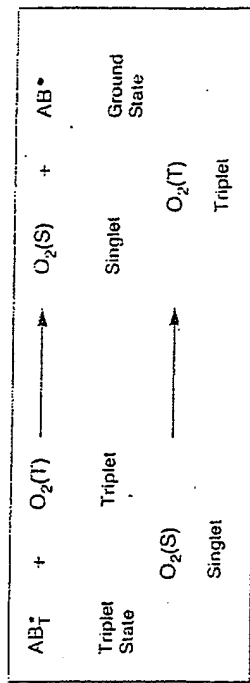
Energy can be transferred to another photoinitiator molecule.

## Transfer

$$AB^*_T + BA^\bullet \longrightarrow AB^\bullet + BA^*_T$$

| Triplet State | Ground State | | Ground State | Triplet State |
|---|---|---|---|---|

**Abstraction**
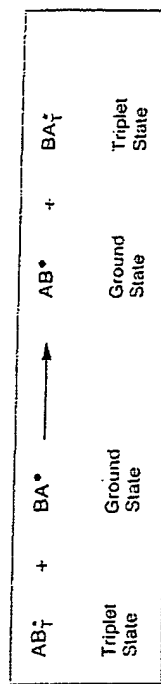
The photoinitiator can loose its energy by forming free radicals, either directly or indirectly. There are many terms used in the coatings industry to describe direct and indirect photo-initiators. The direct type fragments into two (or more) species which are both free radicals, which may or may not initiate polymerisation. The fragmentation giving rise to this type of photoinitiation is commonly called radical cleaving, radical fragmenting or homolytic cission. If cleavage occurs adjacent to the photochemically active carbonyl group, then it is often called an α - cleavage. An example of this type of photoinitiator is acetoxy acetophenone.

**Cleavage**

$$AB^*_T \longrightarrow A^\bullet + B^\bullet$$

Triplet                Free radicals
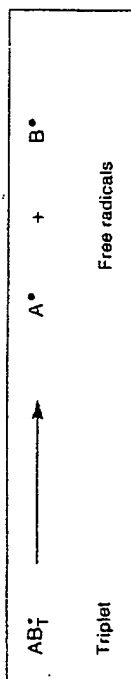
In the indirect type of photoinitiation, a molecule is photochemically excited and abstracts H atom from either another molecule or by an intramolecular reaction to 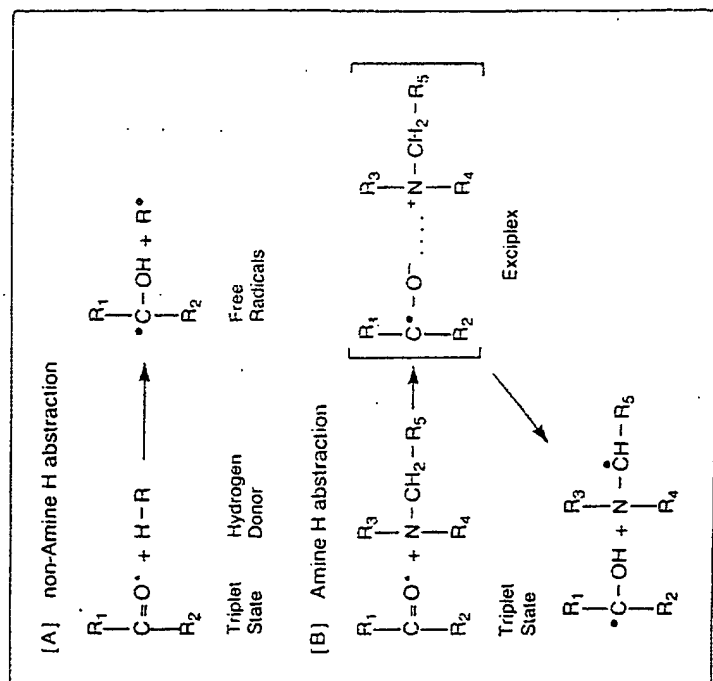form a free radical. The mechanisms involved may be multistep and can be very complicated. Two such mechanisms[4][5][6] are shown below. One involves an amine and here various mechanisms, intermediates and resultant radicals have been proposed[4][5][6][7]. The details of this method of photogeneration will not be considered in any detail here. The reaction shown[4][5] for the amine is considered to be the most likely one to occur.

This class of photoinitiators is commonly referred to as Hydrogen abstractors.

Benzophenone is a typical hydrogen abstractor and photosynergists or co-initiators are typically tertiary amines. The co-initiator may form a complex (exciplex) with the excited state benzophenone, thereby enhancing its reactivity.

It is possible for photoinitiators to undergo both types of photoinitiation and indeed, many commonly used ones are capable of this. However, there is normally a large difference in the rates for each mechanism and the one which predominates is the mechanism by which the photoinitiator is assumed to react.

[A]  non-Amine H abstraction

$$R_1\text{—}C{=}O^\bullet + H\text{—}R \longrightarrow R_1\text{—}\overset{\bullet}{C}\text{—}OH + R^\bullet$$

(with $R_2$)

Triplet State      Hydrogen Donor      Free Radicals

[B]  Amine H abstraction

$$R_1\text{—}C{=}O^\bullet \; + \; R_3\text{—}N\text{—}CH_2\text{—}R_5 \longrightarrow \left[ R_1\text{—}\overset{\bullet}{C}\text{—}O^- \; \cdots \; {}^+N\text{—}CH_2\text{—}R_5 \right]$$

(with $R_2$, $R_4$)          Exciplex

Triplet State

$$\longrightarrow R_1\text{—}\overset{\bullet}{C}\text{—}OH \; + \; R_3\text{—}N\text{—}\overset{\bullet}{C}H\text{—}R_5$$

(with $R_2$, $R_4$)

The Jablonski diagram shown in Figure 2 (from Reference[2]) summarises the interactions of a photon and a potential photoinitiator molecule.

There is sometimes confusion about the role amines perform in a UV curable system. They can fulfil at least two functions. The first (which all amines have) is the ability, to a greater or lesser extent, to reduce oxygen inhibition by donating hydrogen to a peroxy radical to allow the formation of a new radical. This is discussed later. The second function is that of co-initiator or photosynergist. Amines can only act as a photosynergist if they have the correct chemical structure and if a hydrogen abstractor is present. An alternative approach to using free amines is the use of an amine attached to an acrylate prepolymer, which is subsequently polymerised into the coating, thereby reducing its extractability or migration from the coating.
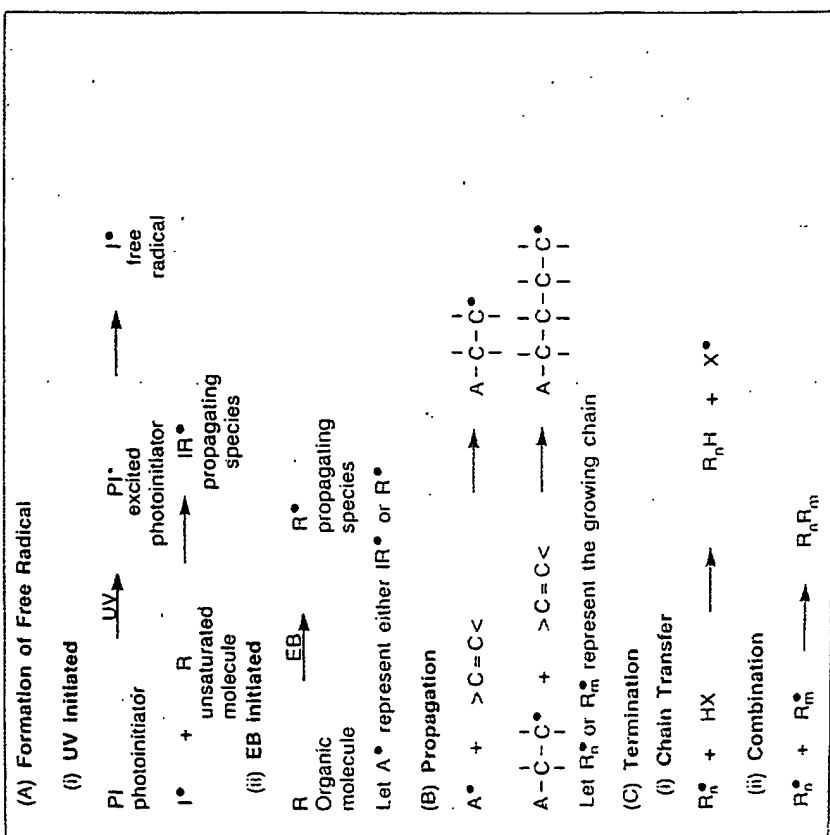
## (A) Formation of Free Radical

### (i) UV Initiated

PI $\xrightarrow{\text{UV}}$ PI* $\longrightarrow$ IR•

PI photoinitiator / PI* excited photoinitiator / I• free radical / IR• propagating species

I• + R unsaturated molecule $\longrightarrow$ IR• propagating species

### (ii) EB Initiated

R $\xrightarrow{\text{EB}}$ R• propagating species

R Organic molecule

Let A• represent either IR• or R•

## (B) Propagation

A• + >C=C< $\longrightarrow$ A–C–C•

A–C–C• + >C=C< $\longrightarrow$ A–C–C–C–C•

Let $R_n^\bullet$ or $R_m^\bullet$ represent the growing chain

## (C) Termination

### (i) Chain Transfer

$R_n^\bullet$ + HX $\longrightarrow$ $R_n$H + X•

### (ii) Combination

$R_n^\bullet$ + $R_m^\bullet$ $\longrightarrow$ $R_nR_m$

**Figure 1 Free Radical Polymerisation Reactions**

The initiation step for UV cure involves the use of photoinitiators which generate free radicals through the interaction of incident UV light. EB cure is initiated by free radicals resulting from the interaction of medium energy electrons bombarding the system. All other steps in the free radical radiation curing process shown in Figure 1 can be described in the same terms (whether UV or EB initiated), namely propagation, chain transfer and termination. For highly efficient systems, such as those in this discussion, the propagation step occurs many times for each occurrence of initiation, chain transfer and termination. Such high efficiency polymerisation is achieved through the use of prepolymers with acrylate functionality, or to a lesser extent, methacrylate, allyl and vinyl functionalities, or internal carbon-carbon double bonds. These functionalities are listed in Figure 2 in decreasing order of reactivity.
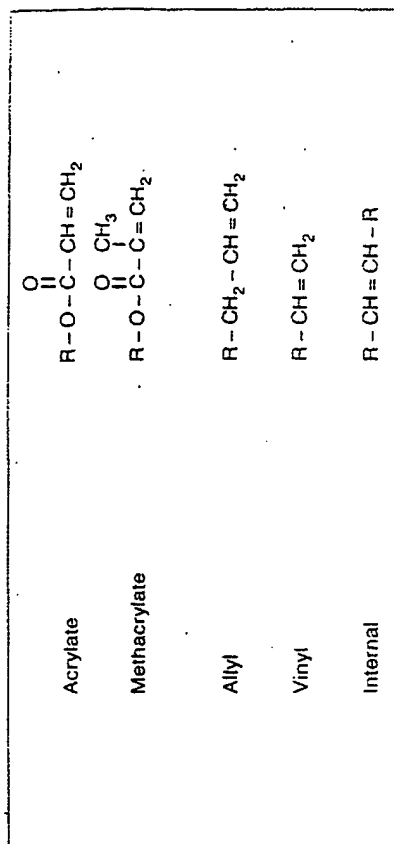
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## (A) [Types of Chemical Functionality]

Acrylate: $R-O-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-CH=CH_2$

Methacrylate: $R-O-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-\overset{\displaystyle CH_3}{\underset{}{C}}=CH_2$

Allyl: $R-CH_2-CH=CH_2$

Vinyl: $R-CH=CH_2$

Internal: $R-CH=CH-R$

**Figure 2 Types of Chemical Functionality**

Oxygen is known to inhibit free radical polymerisation. In the case of radiation curable free radical polymerisation, the two mechanisms proposed for this inhibition are quenching of the excited states of the photoinitiator and the scavenging of free radicals[1]. These reactions are shown in Figure 3 as is the amine synergy one.

## (A) Oxygen Inhibition Reactions

### (i) Quenching reaction.

PI* + $O_2$ $\longrightarrow$ PI + $O_2^\bullet$

excited photoinitiator

### (ii) Scavenging Reaction

R• + $O_2$ $\longrightarrow$ R–O–O•

Strong propagating radical → Weak propagating radical

## (B) Amine Synergy Mechanism

$R_2N-CH-CH_3$ + $O_2$ $\longrightarrow$ $R_2N-\overset{\displaystyle O-O^\bullet}{\underset{}{C}}H-CH_3$

$\longrightarrow$ $R_2N-CH_2-CH_3$

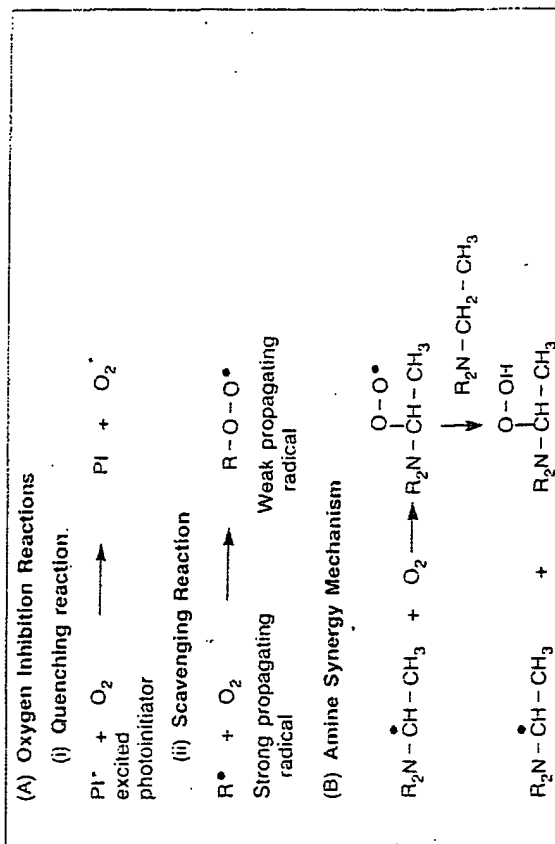$R_2N-\overset{\bullet}{C}H-CH_3$ + $R_2N-\overset{\displaystyle O-OH}{\underset{}{C}}H-CH_3$

**Figure 3 Oxygen Inhibition and Amine Synergy Reactions**